

AD-A105 398

MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF MATERIA--ETC F/6 11/9  
ORIENTATION MEASUREMENTS FROM POLYMER SURFACES USING FOURIER TR--ETC(U)  
SEP 81 K KRISHNAN, S HILL, J P HOBBS N00014-78-C-0676  
TR-4 NL

UNCLASSIFIED

1 - 1  
20  
5 x 5-100



END  
DATE  
FILMED  
0 81  
DTIC

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

1. REPORT NUMBER Technical Report #4	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Orientation Measurements from Polymer Surfaces Using Fourier Transform Infrared Photoacoustic Spectroscopy		5. TYPE OF REPORT & PERIOD COVERED Technical Report
7. AUTHOR(s) K. Krishnan, S. Hill, J.P. Hobbs and C.S.P. Sung		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Materials Science and Engineering M.I.T., Cambridge, MA 02139		8. CONTRACT OR GRANT NUMBER(s) C N00014-78-0676
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy St., Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-699 (472)
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE September 1981
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC ELECTE S OCT 13 1981 D	
18. SUPPLEMENTARY NOTES Prepared for publication in journal. B	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Orientation Photoacoustic Spectroscopy IR internal reflection dichroism Polyethylene terephthalate Fourier Transform IR Spectroscopy Polymer Surface	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Fourier Transform IR Photoacoustic (FTIR-PAS) dichroism studies have been applied to determine molecular orientation from the surface of one-way drawn poly(ethylene terephthalate) film. When compared with ATR dichroic spectra obtained with a modified, rotatable sample holder on the same sample, PA spectra show saturation effects in strong absorption bands near 1730, 1250 and 1100 $\text{cm}^{-1}$ , probably due to the greater penetration depth in the PA technique. The dichroic ratios ( $k_x/k_y$ ) on the plane of	

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

K 300 x/k 100

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

81 10 13 0

AD A105398

DTIC FILE COPY

(block 20, continued)

the sample film have been calculated from PA spectra, only on bands which do not show saturation and compared with the analogous ratios determined from ATR dichroic spectra. For three well-known parallel bands at 1335, 975 and 795  $\text{cm}^{-1}$  the dichroic ratio is greater than unity in both ATR and PAS, as expected from the drawing process. In general, somewhat lower dichroic ratios are observed by PA spectra than by ATR spectra with this sample. Possible reasons for this trend are discussed. This study demonstrates the potential of FTIR-PAS dichroism as a complementary technique to ATR dichroism, especially on samples with rough or brittle surfaces.

12 1000 22 1000  
Office of Naval Research  
Contract N00014-78-0676  
Task No. NR356-699  
Technical Report No. 4

14 TR 1  
Orientation Measurements from Polymer Surfaces  
Using Fourier Transform Infrared Photoacoustic Spectroscopy,

by

K. Krishnan and S. Hill  
Digilab, Division of Bio-Rad Laboratories  
237 Putnam Avenue  
Cambridge, Massachusetts 02139

and

J.P. Hobbs and C.S.P. Sung  
Department of Materials Science and Engineering  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Prepared for publication in journal.

11 September 1981

11 11  
Reproduction in whole or in part is permitted for  
any purpose of the United States Government. This  
document has been approved for public release and  
sale: its distribution is unlimited.

## Abstract

Fourier Transform IR Photoacoustic (FTIR-PAS) dichroism studies have been applied to determine molecular orientation from the surface of one-way drawn poly(ethylene terephthalate) film. When compared with ATR dichroic spectra obtained with a modified, rotatable sample holder on the same sample, PA spectra show saturation effects in strong absorption bands near  $1730$ ,  $1250$  and  $1100\text{ cm}^{-1}$ , probably due to the greater penetration depth in the PA technique. The dichroic ratios ( $k_x/k_y$ ) on the plane of the sample film have been calculated from PA spectra, only on bands which do not show saturation and compared with the analogous ratios determined from ATR dichroic spectra. For three well-known parallel bands at  $1335$ ,  $975$  and  $795\text{ cm}^{-1}$  the dichroic ratio is greater than unity in both ATR and PAS, as expected from the drawing process. In general, somewhat lower dichroic ratios are observed by PA spectra than by ATR spectra with this sample. Possible reasons for this trend are discussed. This study demonstrates the potential of FTIR-PAS dichroism as a complementary technique to ATR dichroism, especially on samples with rough or brittle surfaces.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

Photoacoustic spectroscopy (PAS) has been shown to be a very useful experimental technique for the study of the spectra of gases, liquids, and solids. Rosencwaig(1) has recently reviewed the theoretical and experimental aspects of PAS and has shown its applicability especially for the study of solids. In the PAS experiments the solid under study is placed in a sealed cell containing an inert gas and a highly sensitive microphone. Pulsed or chopped radiation is focussed on the sample by means of suitable optics. If the sample absorbs radiation at any particular frequency, the absorbed radiation is converted into thermal energy by non-radiative processes. This thermal energy is transmitted to the surrounding gas and sets up a pressure wave in the cell. This pressure or acoustic wave is detected by the microphone resulting in the PA signal. This signal is proportional to the incident energy, and is also dependent on the thermal and optical properties of the sample. The thickness or the depth of the sample from which the PA signal emanates is also dependent on the chopping frequency. Rosencwaig(1) has shown that this depth can be of the order of 10 to 100 micrometers at low ( $\sim 5$  KHz) chopping frequencies and of the order of 0.1 to 1 micrometer for high ( $\sim 100$  KHz) chopping frequencies. The PA technique has been recently extended to the mid-infrared region of the electromagnetic spectrum by several investigators using dispersive(2) or Fourier transform(3,4) spectrometers. Krishnan(5) has shown that under normal operating conditions of the Fourier transform infrared (FT-IR) instruments, the PA signal can arise from a layer of thickness around 10 micrometers for typical polymers at  $1000\text{ cm}^{-1}$ . This thickness would then represent an intermediate case when compared to infrared surface measurement techniques such as attenuated total internal reflectance (ATR) and bulk measurement

techniques such as transmission. One of us (Sung,6) has recently shown that the dichroic ratios and hence the surface orientation of polymers could be studied using a modified polarized IR-ATR technique. In this note we show that good quality dichroic spectra can be obtained for polymers using the PA method. The results obtained from PA spectra will be compared with the dichroic ratios obtained for the same sample by the modified polarized ATR technique.

The sample used in the present study was a sheet of poly(ethylene terephthalate), one-way drawn between a pair of rollers. The surface studied was that facing the hot roller. All the spectra presented here were recorded at  $4\text{ cm}^{-1}$  spectral resolution using a Digilab FTS-15 Fourier transform infrared spectrometer. The polarized ATR spectra were recorded using a specially designed accessory with a symmetrical KRS-5 crystal, as described in Reference 6, and a liquid nitrogen cooled mercury cadmium telluride detector. The polarizer in the ATR accessory (a germanium double diamond crossed-plate type from Harrick) was set at perpendicular polarization (TE wave), and two spectra were recorded for the sample oriented with its draw axis perpendicular and parallel to the incident plane. The ratio of peak heights in the two spectra will then yield the dichroic ratio  $k_x/k_y$ , where x is the stretch direction and y is transverse to x. The PA spectra were recorded using a Digilab PAS cell and a gold wire grid polarizer (Perkin-Elmer). Two PAS spectra were recorded, this time by keeping the sample orientation constant but by changing the polarizer orientation by 90 degrees. The ratio of the peak heights in these two spectra will also yield the dichroic ratio  $k_x/k_y$ .

Figure 1 shows the  $k_x$  spectra from the PA (top) and the ATR (bottom) measurements. One can see the qualitative similarity in the appearance of the two spectra. Figure 2 shows the corresponding  $k_y$  spectra.

It can be seen in Figures 1 and 2 that the positions of the strongest bands in the PA and ATR spectra are at different frequencies. This is particularly noticeable for the bands at around 1730, 1250 and 1100  $\text{cm}^{-1}$ . Krishnan(5) has shown that these differences arise due to saturation effects in the PA spectra. When the sample absorption at a particular frequency is very strong, most of the incident radiation at this frequency is absorbed within a sample thickness that is small compared to the thermal diffusion length of the sample and the PA spectrum will show saturation at this frequency(1). The weaker absorptions, however, will not show this effect and will exhibit an apparent increase in intensity relative to the saturated ones. Thus in the PA spectra of the PET sample, the satellite absorbances of the strongest bands in the sample are enhanced, leading to an apparent shift in the strongest bands in the PA spectra. The weaker bands in the PET spectra do not show these saturation effects and appear at the same frequencies in the PA and ATR spectra.

Table 1 summarizes the dichroic ratios  $k_x/k_y$  derived from the PA and the ATR experiments for PET, after excluding saturated bands. It can be observed that for three well known parallel bands(7), at 1335, 975 and 795  $\text{cm}^{-1}$ , the dichroic ratio is greater than unity in both ATR and PAS, as expected from one-way drawing. In hot-rolled samples such as the one used in the present study, the surface may be expected to show a slightly greater degree of orientation than the bulk of the sample. If as was postulated by Krishnan(5), the depth of penetration is greater in the PA experiments than in the ATR experiments, then one would expect the dichroic ratios from the PA spectra to be closer to unity when compared to the ratios from the ATR spectra. The results shown in Table 1 show that this may indeed be the case generally. The results presented here would thus indicate the potential



that polymer orientation as a function of sample depth can be studied by a combination of ATR and PA experiments. Furthermore, if ATR crystals of different refractive indices and effective angles could be used, then a complete depth profiling of the orientation might be achieved.

In conclusion, we have shown that good quality dichroic spectra which give reasonable dichroic ratios can be achieved using the FTIR-PAS technique. As far as the authors are aware, this is the first such study of the dichroic FTIR-PAS spectra. Since the PA technique does not depend on a good contact of the sample with the reflection crystal as in ATR, the PA technique can be used to determine orientation in films with rough or brittle surfaces.

## References

1. Rosencwaig, A.; "Photoacoustics and Photoacoustic Spectroscopy", John Wiley and Sons: New York, 1980.
2. Low, M.J.D.; Parodi, G.A. Infrared Physics 1980, 20, 333; Appl. Spect. 1979, 34, 76.
3. Rockley, M.G. Chem. Phys. Lett. 1979, 68, 455; 1980, 75, 370; Appl. Spect. 1980, 34, 405.
4. Vidrine, D.W. Appl. Spect. 1980, 34, 314.
5. Krishnan, K. Appl. Spect. 1981 (in press).
6. C.S.P. Sung Macromolecules 1981, 14, 591.
7. Jasse, B.; Koenig, J.L. J. Macromol. Chem. 1979, C17(1), 61.

### Acknowledgement

This work was in part supported by the Office of Naval Research. We also acknowledge the generosity of Digilab, who made an FTS-15 available for our ATR dichroism studies. We thank Dr. Willis of ICI (England) for providing the sample PET film used in this study.

Table 1.

Comparison of Dichroic Ratio ( $k_x/k_y$ ) on the PET Surface  
by FTIR-ATR and FTIR-PAS Techniques

Bands ( $\text{cm}^{-1}$ )	Dichroic Ratio ( $k_x/k_y$ )	
	ATR	PAS
1335	6.08	2.56
975	4.09	2.78
795	1.73	1.39

### Figure Captions

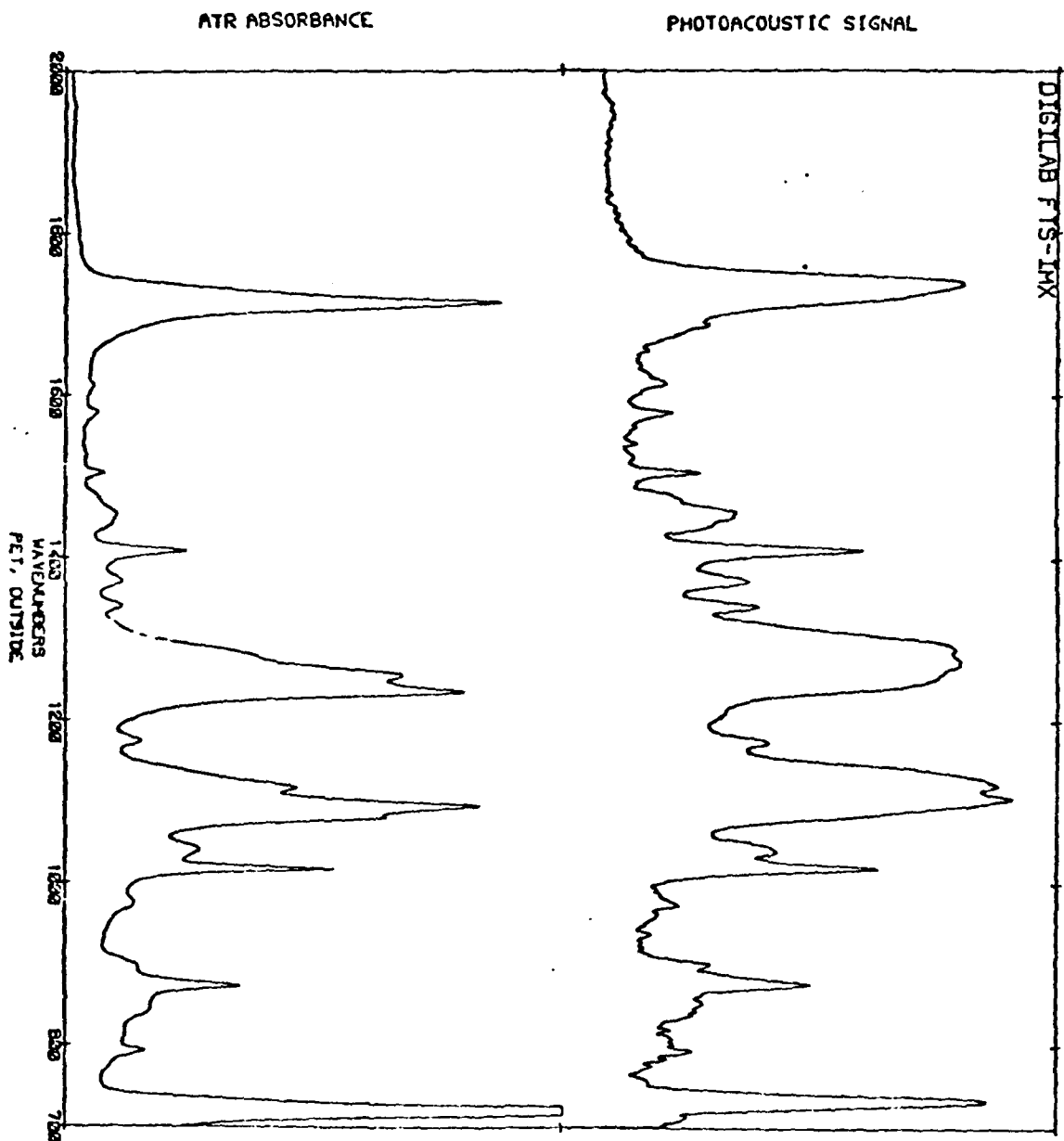
Figure 1. (Top) Photoacoustic spectra of PET surface.

(Bottom) Polarized ATR spectra of PET surface.

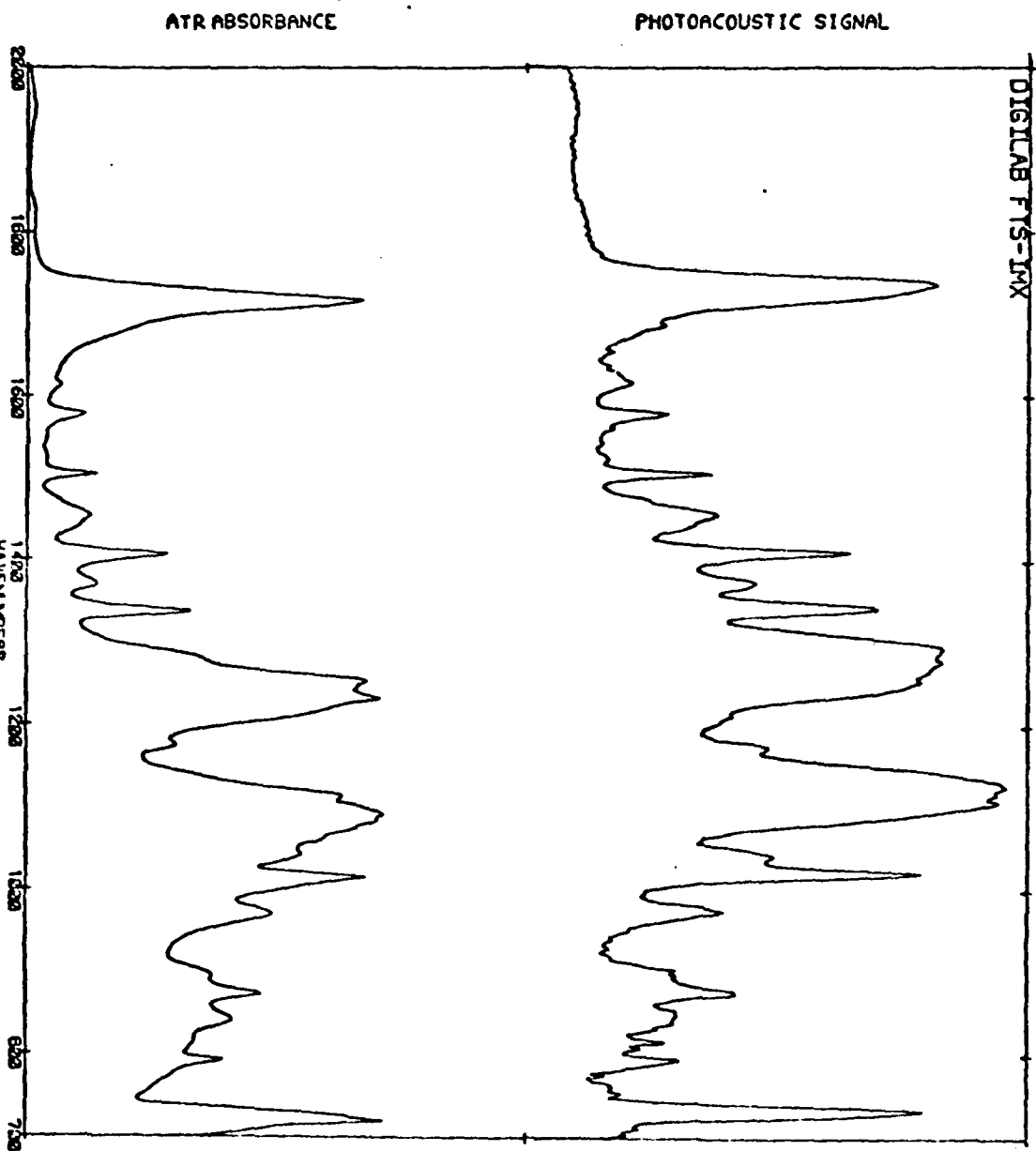
In both spectra, polarization was parallel to x (draw direction) and thus  $k_x$  is obtained.

Figure 2. (Top) Photoacoustic spectra of PET surface.

(Bottom) Polarized ATR spectra of PET surface. In both spectra, polarization was perpendicular to x (draw direction), and thus  $k_y$  is obtained.



PC9-4 OP  
Figure 1



RES-4 DP  
Figure 2

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Stephen H. Carr Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Picatinny Arsenal Attn: A. M. Anzalone, Building 3401 SMUPA-FR-M-D Dover, New Jersey 07801	1
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U.S. Department of Commerce Washington, D.C. 20234	2	Dr. J. K. Gillham Department of Chemistry Princeton University Princeton, New Jersey 08540	1
Professor G. Whitesides Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139		Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. D. R. Uhlmann Department of Metallurgy and Material Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
Naval Surface Weapons Center Attn: Dr. J. M. Augl, Dr. B. Hartman White Oak Silver Spring, Maryland 20910	1	NASA-Lewis Research Center Attn: Dr. T. T. Serofini, MS-49-1 21000 Brookpark Road Cleveland, Ohio 44135	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1	Dr. Charles H. Sherman Code TD 121 Naval Underwater Systems Center New London, Connecticut 06320	1
Professor Ratsuo Ishida Department of Macromolecular Science Case-Western Reserve University Cleveland, Ohio 44106	1	Dr. William Risan Department of Chemistry Brown University Providence, Rhode Island 02192	1
Dr. David Soong Department of Chemical Engineering University of California Berkeley, California 94720		Dr. Alan Gent Department of Physics University of Akron Akron, Ohio 44304	1
Dr. Curtis W. Frank Department of Chemical Engineering Stanford University Stanford, California 94305		Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station D 132 Culver City, California 90230	1



TECHNICAL REPORT DISTRIBUTION LIST, 356A

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. C. Giori IIT Research Institute 10 West 35 Street Chicago, Illinois 60616	1	Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	1
Dr. R. S. Roe Department of Materials Science and Metallurgical Engineering University of Cincinnati Cincinnati, Ohio 45221	1	Dr. R. F. Helmreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	1
Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. R. S. Porter Department of Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01002	1
Dr. T. P. Conlon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1	Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	1
Dr. Martin Kaufmann, Head Materials Research Branch, Code 4542 Naval Weapons Center China Lake, California 93555	1	Dr. Kurt Baum Fluorochem Inc. 680 S. Ayon Avenue Azusa, California 91702	1
Professor S. Senturia Department of Electrical Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Professor C. S. Paik Sung Department of Materials Sciences and Engineering Room 8-109 Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson AFB, Ohio 45433	1	Professor Brian Newman Department of Mechanics and Materials Science Rutgers, The State University Piscataway, New Jersey 08854	1
Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1	Dr. John Lundberg School of Textile Engineering Georgia Institute of Technology Atlanta, Georgia 30332	1
Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	1		

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Western Regional Office Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Eastern Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
		Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.  
Copies

Mr. James Kelley  
DTNSRDC Code 2803  
Annapolis, Maryland 21402

1

Mr. A. M. Anzalone  
Administrative Librarian  
PLASTEC/ARRADCOM  
Bldg 3401  
Dover, New Jersey 07801

1